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Thermally stimulated H emission and diffusion in hydrogenated amorphous silicon

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Abstract – We report first principles *ab initio* density functional calculations of hydrogen dynamics in hydrogenated amorphous silicon. Thermal motion of the host Si atoms drives H diffusion, as we demonstrate by direct simulation and explain with simple models. Si-Si bond centers and Si ring centers are local energy minima as expected. We also describe a new mechanism for breaking Si-H bonds to release free atomic H into the network: fluctuating bond center detachment (FBCD)-assisted diffusion, in which a bond center H may be liberated by intercession of a third nearby Si. H dynamics in a-Si:H is dominated by structural fluctuations intrinsic to the amorphous phase not present in the crystal.

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Introduction. – Hydrogenated amorphous silicon is one of the most important electronic materials, and is used in applications ranging from TFTs in laptop displays to solar photovoltaics and IR imaging/detection. Hydrogen dynamics is key to creation and annihilation of defects and gap states, and is also linked to light-induced degradation [1–4]. Although there have been several studies, a complete picture of H dynamics is not yet available.

A widely held picture posits that unbonded H hops among various attractive sites before capture at a dangling bond [5–10]. An intermediate low-energy pathway involving a metastable dihydride structure has also been reported [11]. However, by calculating hopping rates for different trap sites, Fedders argued that thermal motion of hydrogen does not proceed from dangling bond to dangling bond via bond center (BC) sites and showed diffusion through intermediate levels to be insignificant [12]. In addition, Su *et al.* [13] proposed that Si-H bonds do not spontaneously release H, but rather require the mediation of an external agency: in their case a five-fold or "floating" bond. In crystalline Si, the importance of lattice dynamic activated diffusion has been reported [14,15]. Buda *et al.* [16] has shown diffusion of H in the form of jumps from BC site to another BC via intermediate hexagonal or tetrahedral sites.

Previous work on a-Si and a-Si:H showed that the network dynamics is in some ways quite different from the crystal. In particular, the disorder of the network allows fluctuations in the positions of atoms leading to the interesting observation of "coordination fluctuation". It has been observed in an early first principles simulation that even at $T = 300\,\mathrm{K}$, the number of floating (fivefold) bonds fluctuated between zero and ten in a 216 atom cell, in a 1.8 ps simulation [17]. This work has been updated, and similar effects have been observed in networks including H. It was also found that most of the atoms in the lattice eventually participated in these fluctuations [18].

In this letter, we report an *ab initio* simulation which reveals the role of thermal motion of Si atoms in driving H diffusion. We have undertaken accurate simulations including static lattice simulation (in which Si atoms were frozen) and extended thermal simulation. The static Si lattice simulations shows no H diffusion as compared with the dynamic lattice case, suggesting that the motion of the "Si-sublattice" is important to the H dynamics. A feature of our work is that we determine diffusion mechanisms directly from thermal MD simulation, *not* by imposing a conventional hopping picture among wells (traps) with varying depths. The principal conclusion of the paper is that the dynamic lattice (particularly the motion of pairs or triplets of Si atoms with a BC H present) is a primary means for ejecting atomic H into the network. This mechanism could not be easily inferred from phenomenological kinetic equation models of H transport [12], though it should readily emerge using

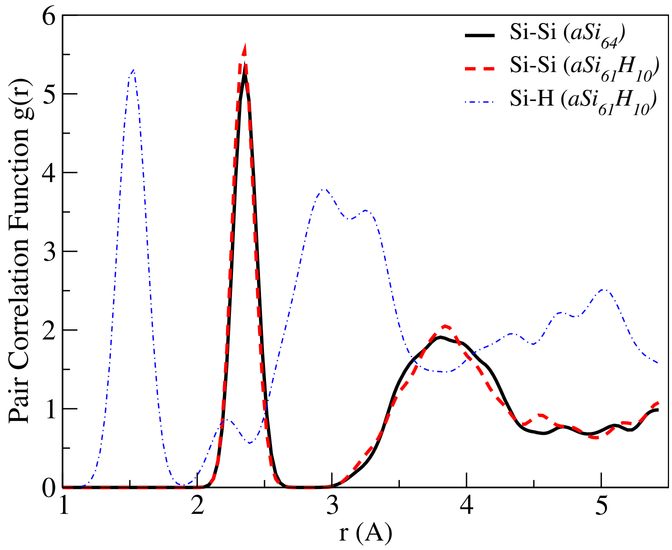

Fig. 1: Si-Si and Si-H partial pair correlation for $aSi_{61}H_{10}$ and Si-Si partial pair correlation for aSi_{64} models.

a method devised to discover rare (long time scale) events like the Activation-Relaxation Technique implemented with *ab initio* interactions [19].

We determine an essential mechanism for H diffusion in the dynamic lattice, namely, “Fluctuating Bond Center Detachment” (FBCD)-assisted diffusion: if the H is initially covalently bonded to a Si atom, it stays bonded with it until another Si comes in the vicinity and makes an instantaneous or fluctuating BC configuration. This event is followed by a switching of H from the covalent bond to the new Si to either form another Si-H bond or hop, depending upon the local environment. This process is important both as a means for the network to generate free H and to create dangling bonds and therefore states within the optical gap. The mechanism we report here is undoubtedly not the sole means of obtaining H diffusion, but is predominant in accurate and relatively extended MD simulations.

Methods. – To understand the diffusion of H at different temperatures we have used a 71-atom model $aSi_{61}H_{10}$. We generated this model by removing three Si atoms from a well-relaxed defect-free aSi_{64} model [20]. We then terminated all the dangling bonds except two with hydrogen. The newly formed supercell is then relaxed using conjugate gradient to form a $aSi_{61}H_{10}$ model (61 Si and 10 H atoms). The computed Si-H partial correlation has the expected peak at 1.5 Å and the Si-Si partial pair correlation show a first peak at 2.35 Å with a subsequent minimum which remains unchanged with hydrogenation as shown in fig. 1. The newly generated model retains a tetrahedral structure and fourfold coordination (for Si) as in the original. We have also considered additional models, a 138 atom model $aSi_{120}H_{18}$ [21] and a 223 atom model $aSi_{214}H_9$ [22][1], and studied H dynamics there to assure ourselves that finite-size effects were unimportant.

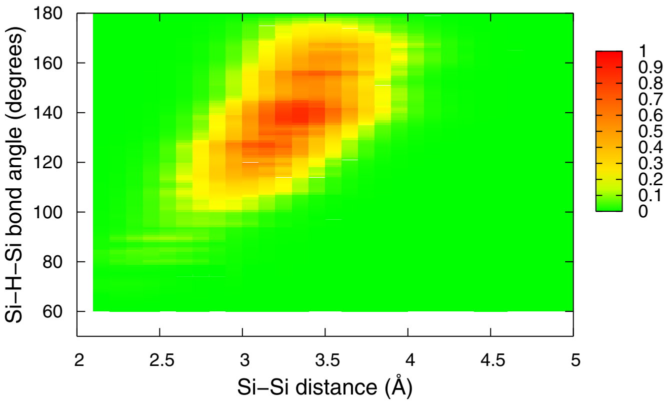

Fig. 2: (Colour on-line) Dynamics of H near BC conformations. The contours give normalized temporal distribution of $R_{\text{Si-Si}}$ as a function of Si-H-Si bond angle from $aSi_{61}H_{10}$ for a total of 6.25 ps at $T = 1000$ K: red, most frequent visitation and green least frequent. The plot is averaged over all H atoms in the cell when in a BC conformation.

The simulations were performed using SIESTA [23] in the generalized gradient approximation for the exchange (GGA) using a parametrization of Perdew, Berke, and Ernzerhof [24]. Norm-conserving Troullier-Martins pseudopotentials [25] factorized in the Kleinman-Bylander form [26] were used. We used a single ζ polarized basis set for Si valence electrons and double ζ polarized basis for H allowing sufficient flexibility in the basis set. We solved the self-consistent Kohn-Sham equations by direct diagonalization of the Hamiltonian and a conventional mixing scheme. Every structural model in this report was relaxed using conjugate gradient (CG) coordinate optimization until the forces on each atom were less than 0.02 eV/Å. The Γ point was used to sample the Brillouin zone in all calculations.

Simulations. – Our strategy has been to study the dynamics of H atoms in small cells which appear to represent the local topology of the amorphous network, using highly accurate methods. The use of such methods precludes simulations much exceeding several picoseconds, particularly because of the small mass of H and the commensurately small time step needed to integrate the equations of motion. In consequence, our conclusions are focused entirely on the *short time* dynamics of the material.

In our simulations, H in a-Si:H is either passivating Si dangling bonds, or occupying other sites, such as BC sites (the most common) or certain other locations that provide energy minima for H. To provide some information

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[1] We removed 9 Si atoms from the aSi_{216} model generated by Barkema *et al.* [20] using a WWW [22] method. We then terminated all the dangling bonds except one with hydrogen. The newly formed supercell is then relaxed well using conjugate gradient to form a $aSi_{214}H_9$ model (214 Si and 9 H atoms).

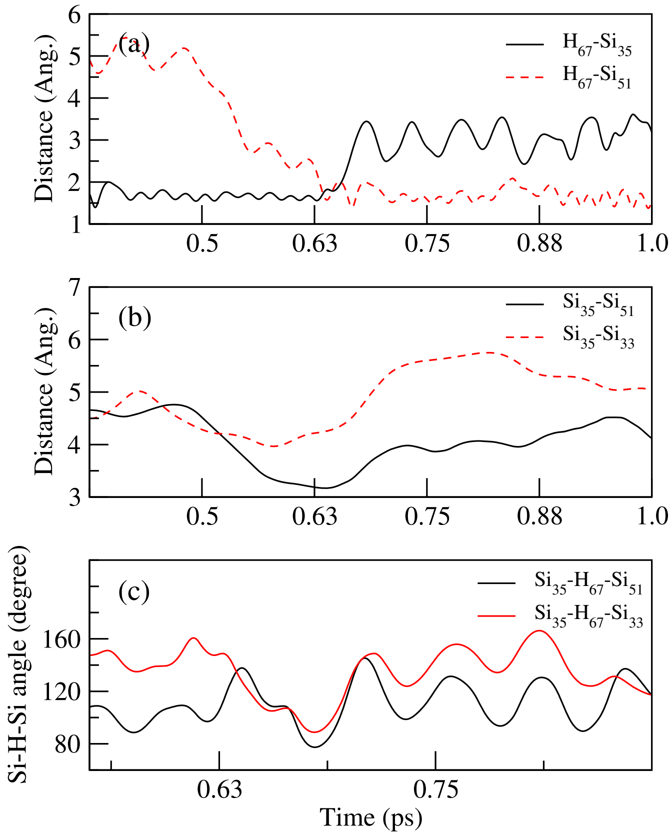

Fig. 3: H_{67} switching the bond from Si_{35} to Si_{51} assisted by the close approach of Si_{33}. a) Shows the switching of the H bond between the two Si. b) and c) show the fluctuation of distances of Si_{33} and Si_{51} from Si_{35} and variation in the corresponding angles centered at H_{67}, respectively.

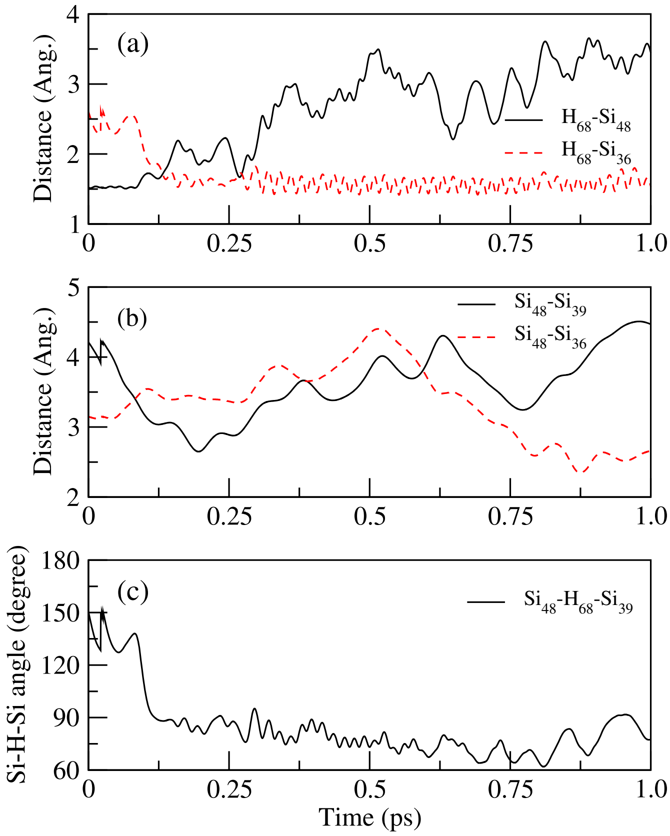

Fig. 4: Another H bond switching event. a) Shows H_{68} switching bond from Si_{48} to Si_{36}. b) and c) show the fluctuation in the distances of Si_{36} and Si_{39} from Si_{48} and variation in the corresponding Si-H-Si angles, respectively.

about the dynamics of our cells, we have considered dynamics near BC conformations in $aSi_{61}H_{10}$. In fig. 2, we have plotted, $\rho(R,\theta) \propto \sum_i \sum_j \delta(R - R_i(t))\delta(\theta - \theta_j(t))$, a distribution function indicating time spent in different parts of the R-θ configuration space, where $R_i(t)$ is the distance between two Si atoms at a time, and $\theta_j(t)$ is the (Si-H-Si) angle formed by two silicons and a central H at a given time. This result shows preferred values of R, ranging from 3.0–4.0 Å and θ (Si-H-Si bond angle) in the range of 110°–180° where the H atoms spends most time. The hydrogen trapping time is highest on the red and lowest on the green regions. Evidently, the energy surface is rather weakly dependent upon θ over a wide range of angles.

To analyze the role of thermally induced Si motion in driving H diffusion, we considered 6.25 ps simulations (25000 MD steps each with time step $\tau = 0.25$ fs) for $aSi_{61}H_{10}$ at $T = 300$ K and $T = 1000$ K. The difference in the H diffusion for these two cases is easily extracted from the time-averaged mean squared displacement of H, which is defined as $\langle\sigma^2\rangle_{\text{time}} = \frac{1}{N_{MD}N_H}\sum_{t=1}^{N_{MD}}\sum_{i=1}^{N_H}|\vec{r}_i(t) - \vec{r}_i(0)|^2$, where N_{MD} is the total number of MD step, N_H and $\vec{r}_i(t)$ are total number and coordinates of H at time t, respectively. This yielded an average mean square displacement of 0.14 $Å^2$ for $T = 300$ K and 1.06 $Å^2$ for $T = 1000$ K. Similar analysis on Si gives an average mean square displacement of 0.06 $Å^2$ and 0.57 $Å^2$ for $T = 300$ K and $T = 1000$ K, respectively.

Discussion. – In the case of $aSi_{61}H_{10}$ at $T = 1000$ K, we have observed 9 bond-breaking events which are accompanied by rapid bond switching in the 6.25 ps simulation. For $aSi_{214}H_9$ at 300 K we have observed 5 bond-breaking events in the 10 ps simulation time; all are FBCD assisted. Only one bond breaking event was observed for $aSi_{61}H_{10}$ at 300 K for the total simulation time of 6.25 ps. After the bond breaking, all of the events lead to the hydrogen passivating a dangling bond. To discuss the FBCD mechanism in detail, we have selected two H from $aSi_{61}H_{10}$ model namely H_{67} and H_{68} at $T = 1000$ K, which diffuse through FBCD. To analyze the role of the thermal motion of the neighboring Si atoms we tracked all nearby Si pairs correlated with the motion of H in both cases.

In fig. 3, we show a situation in which H_{67} initially bonded to Si_{35} switched to Si_{51}. This event follows the close approach of Si_{51} and Si_{33} to the Si_{35}-H_{67} bond and forms a fluctuating bond center conformation. As the distance Si_{35}-Si_{51} and Si_{35}-Si_{33} change from 4.8 Å to

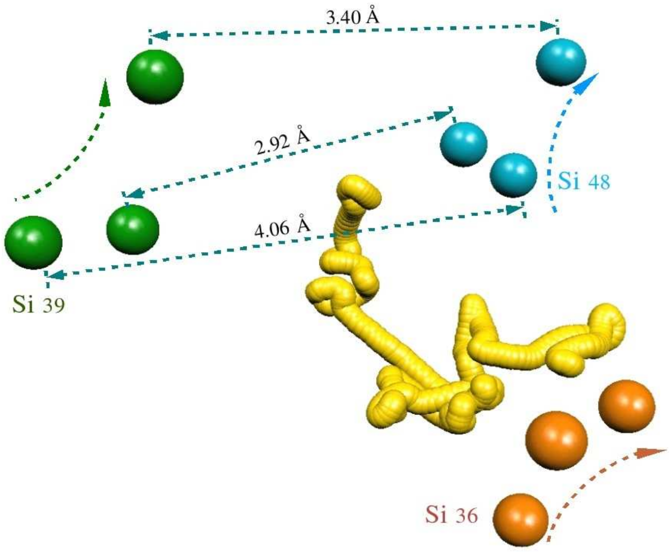

Fig. 5: (Colour on-line) Fluctuating Bond Center Detachment and diffusion. Trajectory (averaged over 400 steps) of H_{68} are shown in yellow, while Si_{48}, Si_{36}, and Si_{39} are shown with blue, orange, and green colors respectively for three different time steps of the simulation.

3.1 Å and from 5.0 Å to 4.0 Å, respectively, as shown in fig. 3(b), the bond angle Si_{35}-H_{67}-Si_{51} changes from 140° to 80°. At the same time, the bond angle Si_{35}-H_{67}-Si_{33} also changes from 160° to 95°. These introduce change from a BC configuration, which is a local energy minimum, to the energetically unstable part of the R-θ configuration space, compelling H to diffuse and form a bond with another Si.

A second case for the FBCD-assisted diffusion involves H_{68} similar to the previous example. As shown in fig. 4(a), we observed a bond-breaking process in H_{68}, a situation where H_{68} which was initially bonded to Si_{48} and later switched to Si_{36}. The switching occurs due to the close approach of Si_{39} to the Si_{48}-H_{68} bond and forms a fluctuating bond center conformation. As the distance Si_{48}-Si_{39} changes from 4.2 Å to 3.0 Å as shown in fig. 4(b), the bond angle Si_{48}-H_{68}-Si_{39} changes from a bond center configuration 150° to 89°, compelling the H to diffuse and form a bond with another Si. Figure 4(c) shows the time-dependence of the Si-H-Si bond angle. The bond angle undergoes a significant shift near the bond-switching event, as one can deduce by comparing to fig. 4(a) and fig. 4(b).

In fig. 5, we show the trajectory of H_{68} in FBCD-assisted diffusion. The average positions of H_{68} are shown in yellow, while Si_{48}, Si_{36}, and Si_{39} are shown with blue, orange, and green colors, respectively at three different time steps of the simulation. H_{68} is initially bonded to Si_{48}, becomes a fluctuating bond center H with approach of Si_{39}, is ejected and eventually bonds to Si_{36}.

The FBCD mechanism is reminiscent of that of Su *et al.* [13], also depending upon the intercession of a Si not part of the initial conformation. However, the FBCD is a more general process that may or may not increase the Si coordination. We found many cases of H detachment in which no Si was overcoordinated. Ejection of H is a more subtle process than just changing coordination, and depends on the the local geometry (R, θ). Finally, all such FBCD conformations arise from fluctuations, and are thus short lived [17]. The mechanism of Su *et al.* is a special case of FBCD.

In conclusion, we have demonstrated the nature of H diffusion in a-Si:H by direct simulation and with the aid of a model to develop a fairly simple picture of H motion. H emission is stimulated by Si motion, and the FBCD mechanism is shown to be important both for stripping off H chemically bonded to Si (thus creating "free" atomic H), and of course for creating Si dangling bonds. Our work is consistent with analogous studies in c-Si [16], and is a generalization of the work of Su and Pantiledes [13].

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